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Influence of droplet size on the release of atomic sodium during the combustion of black liquor

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Abstract

This paper reports on the implementation of a quantitative planar laser-induced fluorescence (PLIF), which employs an absorption technique simultaneously, to assess the effect of initial diameter on the release of atomic sodium. The temporal release of the atomic sodium under fuel rich conditions was found to be different from that under fuel lean conditions, especially during the smelt coalescence stage. The total atomic sodium released and the release rate of atomic sodium increase as the initial diameter of the black liquor droplet is decreased. This highlights the role of small droplets, possibly derived from ejecta, in fume formation.

Keywords: Black liquor, Sodium, Droplet size.

1. Introduction

Black liquor is a by-product in the kraft pulping process and has very high sodium content, typically 15–25 wt% (dry). The sodium can be chemically bound to either organic or inorganic compounds in the black liquor [1]. Black liquor is most commonly burned in a recovery boiler to recover the sodium-based pulping chemical. One of the major problems in a recovery boiler is the deposition of inorganic material, mainly sodium compounds, in the upper furnace causing fouling and corrosion. This deposition reduces the effectiveness of heat transfer and causes material failure and unexpected shutdown, which reduces the overall efficiency of the pulp and paper mills [2]. The origin of the deposition can be divided into three categories: carryover particles, intermediate-size particles (ISP) and submicron fume [2–3]. The carryover particles result from the physical entrainment of the small black liquor droplets (0.1–2 mm) into the furnace gases, which burn in the upper furnace [3–5]. The ISP (1–100 μm) results from physical ejection during black liquor combustion [4, 6]. The formation of fume (<1 μm) is due to the reaction of evolved sodium vapour with the combustion gases in the furnace to form sodium carbonate (Na_2CO_3) and sodium sulphate (Na_2SO_4) [6–9]. The recent mill study by Tamminen et al. [10] shows that most of the fuming occurs during the in-flight burning of black liquor droplets and only a small part of the fume originates from the char bed. Mathematical models (CFD) of deposition and fume formation [2–3, 11–12] have been developed with a view to optimising these processes. However, there is a need for these models to be improved, which requires reliable data of the release of sodium.

The combustion of a single black liquor droplet can be divided into the four stages of drying, devolatilisation, char combustion and smelt oxidation [13]. Most studies of the release of sodium during the combustion of black liquor have been conducted in closed furnaces, which have the advantage of providing a well-defined gaseous environment and temperature field [4, 6, 8–9, 14–15]. Frederick and Hupa [15] suggested that the sodium loss during devolatilisation is the most significant source of sodium contributing to fume formation. However, Li and van Heiningen [9] have proposed that the most significant release of sodium vapour occurs during the char combustion stage and is due to the reduction of Na_2CO_3 by carbon. The study by Cameron [8] concluded that significant amounts of sodium vapour are released during the smelt oxidation stage due to the reaction between Na_2S and Na_2CO_3. Later, the study by Verrill et al. [6] identified that a significant release of sodium during the devolatilisation stage is caused by the physical ejection of droplet fragments. The physical ejection mechanism can also occur during the char combustion stage under oxidising environments [4, 14] and the smelt oxidation stage [13]. This ‘ejecta’ or ISP undergoes char combustion and smelt oxidation (as described above) in the free board above the bed to release sodium into the upper furnace. Other researchers have used chemical equilibrium approaches to predict the fume formation in the lower furnace. The major sodium species in the gas phase within this region are Na (g) and NaOH (g) [7, 16]. These studies suggest that atomic sodium could be a major contributor to fume formation. None of those previous investigations, however, provide the temporal history of the release

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of sodium during the black liquor combustion because sodium vapour is unstable and cannot be measured directly in the outlet gases from those reactors or obtained from chemical equilibrium calculations.

Previously, Verrill and Wessel [3] have modelled both the influence of droplet size and furnace temperature on the sodium loss from physical ejection. However, this model is yet to be validated due to the lack of suitable experimental data. More recently, the quantitative in-situ measurement of atomic sodium released from a burning black liquor droplet in a flat flame was conducted by Saw et al. [17] using a simultaneous planar laser-induced fluorescence (PLIF) and absorption technique. They also measured droplet surface temperature by images of the natural (filtered) luminosity of the droplet [18]. No physical ejection from either technique, both of which are sensitive to it, was detected during any of the stages of combustion in this flame. The lack of ejecta was further evidenced by the analysis of sodium left in the residue, found to be less than 2% after 20 s of combustion in the flame [17]. The ability to avoid physical ejection has scientific advantages, since it allows the combustion and ejection processes to be isolated. The temporal history of the release of atomic sodium from the combustion of a black liquor droplet can thus be assessed directly using this PLIF technique. However, to date no such investigations have been reported on the influence of droplet size in a flame or in a closed furnace environment. The aim of the present study is thus to assess the influence of initial droplet diameter on the release of atomic sodium during each stage of black liquor combustion.

2. Methodology

A consistent quantity of black liquor (10 mg with an initial diameter, d_i = 2.0–2.3 mm) was carefully applied to a loop (3 mm diameter) of a platinum wire (0.5 mm diameter). The composition of the black liquor, obtained from a Swedish pulp mill, is shown in Table 1. The loop with the black liquor droplet was placed 10 mm ± 1 mm above the tip of the flat flame burner, using a retort stand. The black liquor was burned in the flame provided by a flat flame burner at three conditions, two fuel lean at $Ø_{bg}$ = 0.8, 0.9 and the other one fuel rich at $Ø_{bg}$ = 1.25. Note that the symbol $Ø_{bg}$ denotes the equivalence ratio of the burner gases alone, which were held constant through a given experiment, and ignores the contribution of the black liquor droplet to the fuel, which varies throughout the experiment. The flat flame burner comprised a matrix of small diffusion flames with the total burner having dimensions of 80 mm × 100 mm. The burner was fed with local natural gas as the fuel and the compressed air was supplied by our laboratory compressor. The total flow rate of fuel and air to the burner was 65.8 *l*/min (STP). A co-flow of air was supplied around the flat flame burner to stabilize the flame from flicker. The experiment was then repeated with black liquor of 5 mg (d_i = 1.5–1.9 mm) and 2 mg (d_i = 1.1–1.4 mm).

Table 2 The elemental composition of the black liquor, given as a percentage of dry solid content.

Chemical analysis	Weight - % of DS
Carbon	30.30
Hydrogen	3.50
Nitrogen	0.20
Sulphur	3.74
Sodium	22.00
Potassium	1.59
Chlorine	0.05
Oxygen (by balance)	38.60

The gas flame temperature, $T_{gf,35}$ was measured using a 0.5 mm diameter Type-R (Pt/Pt-13% Rh) thermocouple at the centreline, and at a vertical height of 35 mm, without the burning droplet for $Ø_{bg}$ = 0.8 was 1600°C and 1725°C for $Ø_{bg}$ = 1.25. The measured temperatures were corrected for radiation losses from the thermocouple using the radiation correction equation of Brohez et al. [19].

The laser and optical arrangement in the present study is similar to that of Saw et al. [17]. Two-dimensional images were obtained using simultaneous PLIF and absorption with the arrangement shown in Fig. 1. A tuneable dye laser (Lambda Physik, Scanmate), was pumped by a Nd: YAG (Quantel, Brilliant b) laser. The dye laser was scanned around 588–590 nm to excite the D_1 and D_2 sodium lines at 589.59 nm and 589 nm, respectively. All the measurements were performed using the D_1 line because of the strong beam absorption observed with the D_2 line. The output radiation was directed to appropriate cylindrical lenses to form a sheet of light (40 mm × 3 mm) through the flat flame, located between two glass cells containing fluorescent dye. The pulse-to-pulse energy variation was measured to be about 12%. The PLIF signal from the sodium atoms was collected using a gated intensified CCD camera (Princeton Instruments ICCD-576) aligned orthogonal to the laser sheet. A gate width of 10 ns was selected to minimise noise and background radiation from the flame. Images were recorded at five images per second. A polariser was placed in the front of the ICCD camera lens to minimize any elastic laser scattering processes. No signal was observed when the polarisation axis of the polariser was set perpendicular to the laser polarisation axis. For absorption measurements, the incoming and outgoing laser intensity was obtained from the two dye cells calibrated for laser intensity. Measurements were taken about 15 mm above the black liquor droplet to avoid the scattered light from the particle and the platinum wire.

The present study was performed to understand the temporal history of the release of atomic sodium from ignition until the burn-out of the liquor. The images from the SLR camera were used to measure

the duration of the drying, devolatilisation, char consumption and smelt coalescence stages. The characteristic of black liquor combustion stages are described in Ref. 18. Note that the term char consumption is used instead of char combustion because the char is consumed predominantly by CO_2 and H_2O in this flat flame environment (Saw et al. [18]). The first three stages were easily detectable but the last stage of smelt oxidation, distinct by the intense glow of salt residue [13], could not be separated from the glow of the salt itself at the high temperature. However, the smelt coalescence time was considered to be from the end of the char consumption stage until the signal of the concentration of atomic sodium or residual disappeared. For the case $Ø_{bg}$ = 0.8 of d_i > 1.5 mm, some extrapolation was required to determine the duration of the smelt coalescence stage due to the limitation in the capture of 780 s owing to the memory capacity.

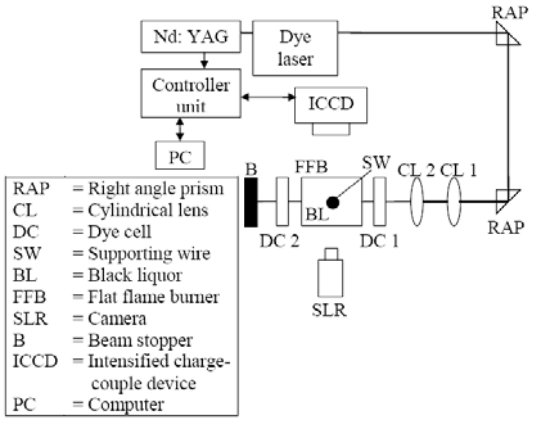

Fig. 1. The experimental apparatus (plan view) used to image atomic sodium by PLIF and also absorption, during the combustion of a black liquor droplet.

3. Result and Discussion

Figure 2 compares the concentration of atomic sodium in the plume at three $Ø_{bg}$ for the initial diameter, d_i = 1.3 mm. Each of the points in the lines shown in Fig. 4 were averaged over five pixel matrix (5 × 1) at the centre-line of the sodium plume, at an axial distance of 35 mm above the black liquor droplet. Note that the temporal history of the atomic sodium release times, t, is normalised by the total combustion time, t_{tot}. As expected, the concentration of atomic sodium under reducing conditions is higher than that under oxidising conditions. Under fuel rich conditions, the majority of the evolved sodium remains in elemental form [20]. Nevertheless, some sodium hydroxide can be formed under these conditions via (1) due to the presence of water vapour in the flat flame. Under fuel lean conditions, the reduction of H-atom level is favoured to produce NaOH, as shown in (1), and the presence of oxygen converts atomic sodium to sodium oxide (NaO) and sodium dioxide (NaO_2) [21]. The peak concentration of atomic concentration for $Ø_{bg}$ = 1.25 was found to be higher than that for $Ø_{bg}$ = 0.8 by factor of 3 and 2.5 for $Ø_{bg}$ = 0.9.

$$Na_{(g)} + H_2O_{(g)} \leftrightarrow NaOH_{(g)} + H_{(g)} \qquad (1)$$

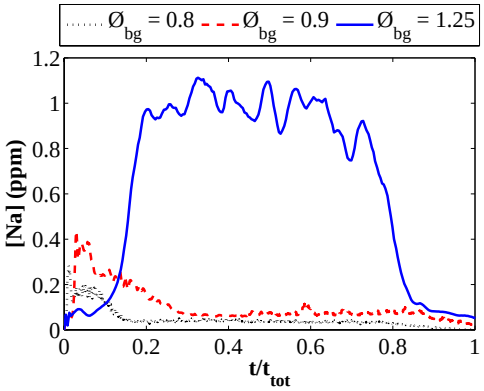

Fig. 2. The concentration of atomic sodium in the plume at three flame conditions for the initial diameter, d_i =1.3 mm.

Figure 3 presents the influence of d_i on the release rate of atomic sodium for $Ø_{bg}$ = 0.8, 0.9 and 1.25. Note that the release rate of the atomic sodium was calculated from the total atomic sodium released relative to its combustion time at the end of each combustion stage. Details of the combustion time and the total sodium released are discussed in Ref. 22. The release rate of atomic sodium is greatest under fuel rich conditions. Overall, the release rate of atomic sodium decreases parabolically as d_i is increased during the initial three stages of combustion. This can be explained by the ratio of surface area to volume decreasing with d_i. The release rate of atomic sodium during the char consumption stage was found to be 1.5 to 2 times larger than that during the devolatilisation stage and 2 to 4 times larger than that during the drying stage. Note that lines, as shown in Fig. 3, are provided as a guide only. More data is required to identify the exact nature of the relationship. Significantly, the release rate of atomic sodium during the smelt coalescence stage for $Ø_{bg}$ = 1.25 is greatest by at least an order of magnitude. However, the release rate of atomic sodium during the smelt coalescence stage was found to be 20% slower than that during the char consumption for $Ø_{bg}$ = 0.8.

The release rate of atomic sodium during the smelt coalescence stage was found to be almost independent from d_i, as shown in Fig. 3d. The release rate during this stage was found to be at least an order of magnitude higher than that during the initial three stages of black liquor combustion. While, the extensive release of atomic sodium from the sodium salt residue at high temperature after the char consumption stage occurs in a relatively small percentage of the mass of the black liquor in a recovery boiler, the effect could still be significant in fume formation. While such fine droplets may constitute a small mass fraction of the liquor flux, it can lead to a large number of fine particles.

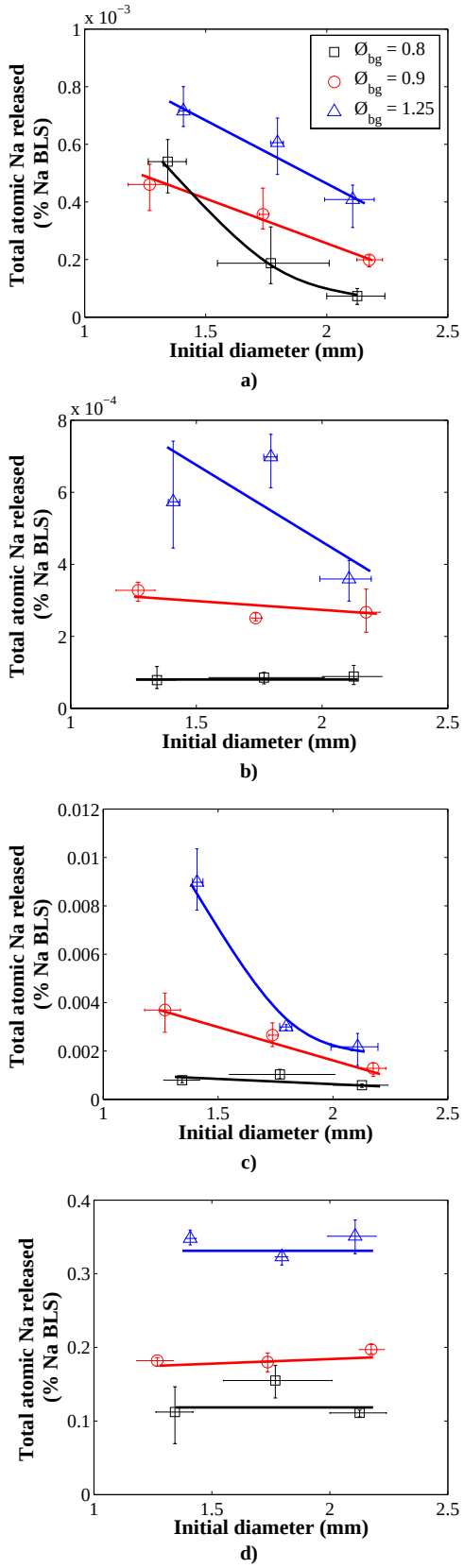

Fig. 3. The influence of initial diameter on the release rate of atomic sodium during the stages of a) drying; b) devolatilisation; c) char consumption and; d) smelt coalescence for $Ø_{bg}$ = 0.8, 0.9 and 1.25.

4. Conclusion

The influence of initial droplet on the release of atomic sodium during each stage of the black liquor combustions using PLIF technique has been assessed. The release rate of atomic sodium is dependent upon initial droplet diameter. It decreases with an increase with d_i to the second power during the initial three stages of black liquor combustion. This highlights the importance in fume formation of small droplets, typically formed as ejecta in black liquor recovery boilers. It suggests that significant fume formation can occur during the in-flight combustion of the carryover or the ejecta due to the significant release of atomic sodium.

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